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Research Paper

CO₂-argon-steam oxy-fuel (CARSOXY) combustion for CCS inert gas atmospheres in gas turbines

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HIGHLIGHTS

- Integration of CCS system, oxy-fuel combustion in Humidified Gas Turbines.
- Optimum CARSOXY blend proposed for gas turbine combustors.
- CO₂ concentration increased for further capture and NO_x eliminated.
- Numerical model successfully used with optimum blend.

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ABSTRACT

CO₂ emitted from gas turbines in power plants is considered a major contributor to the global environmental damage. Carbon Capture and Storage (CCS) integrated with oxy-fuel (OF) combustion is an advanced and innovative approach that may be used in turbines to reduce these emissions. This method is based on CO₂ recycling, however the obstacle to using this recirculation approach in gas turbines is reduction in their performance and reliability.

This paper attempts to address the problem in a novel way by investigating theoretically a number of blends that can overcome the performance and reliability issues of pure CO₂. These blends, comprising of argon, H₂O and CO₂, can be used as a working fluid with oxygen and methane as reactants. Additionally, a numerical model for an industrial gas turbine is employed. The aim is to find the optimum blend for complete NO_x elimination with a recirculation of products. This study uses 0-D chemical kinetic software (Gaseq), an empirical selection approach with design of experiments and, 1-D chemical kinetic software (CHEMKIN-PRO).

Results identify the optimum blend which is numerically assessed in an industrial gas turbine that has been experimentally correlated. The efficiency of this turbine running the selected blend is 1.75–13.93% higher than when running with natural gas/air conditions. This shows the promising use of this blend for a future high efficiency CCS-Oxyfuel approach in gas turbine combustors.

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1. Introduction

Increasing demand for energy production from fossil fuel-fired electrical plants significantly raises anthropogenic emissions of CO₂, with its inherent consequences for climate change [1]. The

dependency on gas turbines in the power sector has been vastly increasing because of their versatility in covering a wide range of energy load demands [2]. In gas-turbine combustors, different advanced technologies have been investigated to mitigate CO₂ emissions and other pollutants to maintain a clean environment [3].

Carbon Capture and Storage (CCS) has been proposed as one of the most innovative technologies utilised to mitigate emitted CO₂

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Nomenclature

G_i^0	molar free energy at the atmospheric pressure of species i [J/mole]	ϕ	equivalence ratio [–]
x_i	equilibrium number of moles of species i	η_{CC}	efficiency of a combustion chamber
G	Gibbs free energy [J]	η_{pC}	polytropic efficiency of a compressor
n_{Sp}	species n	η_{pT}	polytropic efficiency of a turbine
p	pressure [Pa]	η_m	mechanical efficiency
T	temperature [K]	Π_C	compressor pressure ratio
R	universal gas constant [J/mole K]	Π_T	turbine pressure ratio
c_p	specific heat at constant pressure [kJ/kg K]	M	cooling air distribution factor
h_{fuel}	specific enthalpy of fuel at combustion chamber inlet [kJ/kg]	q_{in}	amount of input heat [kJ/kg]
L_T	gas turbine specific work [kJ/kg]	$\bar{c}_{p_{gas-air(3-4)}}$	averaged value of gas specific heat through the expansion [kJ/kg K]
L_c	specific work of compression [kJ/kg]	$\bar{c}_{p_{air(1-2)}}$	averaged value of air specific heat through the compression [kJ/kg K]
LHV	lower heating value [kJ/kg]	T_2	outlet compressor temperature [K]
T_0	ambient temperature [K]	T_{3t}	inlet turbine temperature [K]
T_1	inlet compressor temperature [K]	η_{GT}	gas turbine plant efficiency
r_{air}	cooling air mass flow and compressor inlet mass flow ratio		

from fossil-fueled power generation stations [4]. Basically, CCS is an approach through which CO_2 is captured from large industrial sources, such as gas turbines in power plants, and deposited securely into safe locations, such as subterranean sites, to protect the global environment [5]. Oxyfuel (OF) combustion is a promising technique which can be combined with CCS to enhance the combustion efficiency for the power cycle [6]. This technique involves burning hydrocarbon in a highly-diluted atmosphere at near-stoichiometric conditions, leading to high chamber temperatures. Consequently, a portion of the CO_2 from the flue gas is employed in a recirculation process to control combustor temperature. The remaining CO_2 can be treated for further applications [7].

A drawback of the recirculation of CO_2 in gas-turbine combustors is a reduction in both overall efficiency and generated output power [8]. Practically, the cycle performance can be improved by about 15% through employing a humidified working fluid in a combustor [9]. In Humid Air Turbines (HAT), the efficiency and output power are enhanced by humidifying the compressed air [10]. The Evaporative Gas Turbines (EvGt) cycle, representing one of the configurations of the HAT cycles, was integrated with oxyfuel combustion. The aim was to improve the performance of the cycle while reducing emitted NO_x , in comparison with a combined cycle [11]. However, this enhancement in turbine performance is limited because water injection into a combustion process increases blow-out propensity. This can lead to a shutdown of the system [12].

To avoid this issue, it is proposed in this study to add another gas with CO_2 - H_2O mixture in a gas combustor using an EvGt cycle. This should enhance the efficiency by improving thermodynamic properties of the working fluid such as, specific heat ratio (γ). Thus, equivalent power and efficiency to that of a conventional cycle should be produced.

Moreover, a novel approach is suggested in this paper to use a combination of concepts which not only integrate CCS technologies with oxyfuel combustion and EvGT cycle, but also add to the working fluid inert gases (i.e. Argon) to the mixture of CO_2 and water, thus improving the thermodynamic properties of such a blend. The aim of this investigation is to find the optimum gas blend that can replace air as a working fluid. Argon is used in these blends due to its higher specific heat ratio and because of its relatively high concentration in the atmosphere. Thus, gas turbines using the suggested blend could produce higher efficiency than that of a conventional air cycle. The blend of Argon- CO_2 - H_2O in a pure domain of

oxygen heightens the improvement in the cycle efficiency and reduces flame blowout. Meanwhile, a CO_2 recirculation approach can be utilised in gas turbines to maintain a clean environment.

This paper theoretically investigates a considerable number of CO_2 , Argon and Steam with OXYfuel combustion (CARSOXY) blends. The goal is to discover the blend that has similar thermodynamic properties to air while recycling CO_2 and emitting zero NO_x . The proposed cycle for this technology is depicted in Fig. 1. A mathematical program is used to calculate the generated output power and the efficiency of an industrial gas turbine running the optimum blend with oxygen and methane, compared with Natural Gas (NG)/air.

2. Setup

The investigation process included four steps used to detect the optimum blend that has similar thermodynamic characteristics to air as a working fluid. This optimum blend can be used in a combustion process for gas turbines to generate equivalent power to that of current cycles while reducing emissions and pollutants.

This process was started using a 0-D chemical kinetic software (Gaseq). This program is based on a method of complex balance at specified pressure, which was defined by Sanford Gordon and Bonnie J. McBride for NASA [13]. Eq. (1) shows the Gibbs free energy equation for n species which is used to calculate the products:

$$\frac{G}{RT} = \sum_{i=1}^{n_{Sp}} \left(\frac{x_i G_i^0}{RT} + x_i \ln \frac{x_i}{\sum x_i} + x_i \ln p \right) \quad (1)$$

First, Gaseq was utilised to generate 120 blends of argon, H_2O and CO_2 in an oxygen atmosphere with methane as a fuel at 10 bar and 900 K, which may be considered to be industrial operation conditions. Simultaneously, the properties of the products for each blend, such as outlet temperature, γ and heat capacity (c_p), were calculated. Moreover, the mole fractions were determined for both CO_2 and water vapor as products. An adiabatic process was considered for the combustion chamber. Each blend was represented by its number and an acronym (X, Y, and Z) in which “X” stands for the molar fraction of argon, “Y” for H_2O and “Z” for CO_2 . The remaining fractions were used for oxygen and methane at a range of equivalence ratios which is between 0.67–1.00.

Second, empirical data obtained from the Gaseq program was used to compare each blend with a reference, which was a conven-

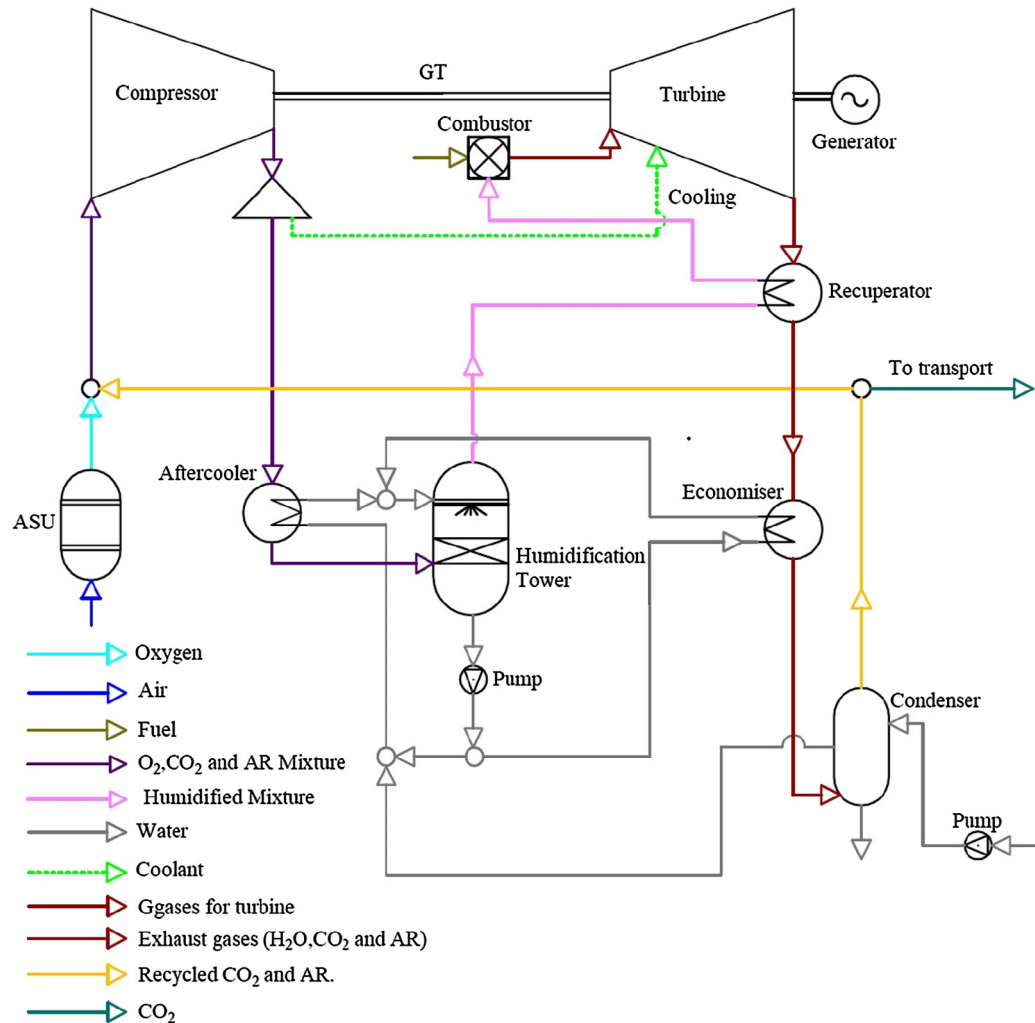


Fig. 1. Schematic diagram of the proposed cycle.

tional air-fuel mixture. Through this process, four equivalent intervals were used to divide between the greatest and the smallest value for each property of these blends. Every interval with a value higher than the reference was signed (+), whereas (–) identified those lower than the reference.

At this stage, a Design of Experiment (DOE) was devised to provide a minimal number of experimental layouts. Minitab software was employed as a tool for DOE, by applying a two-level full factorial design due to the number of inputs. Therefore, there were eight combinations of these blends' components, showing the correlation between them and their products. As such, reliable conclusions can be proposed through matrices obtained by following this systematic procedure [14]. At the same time, the expense and effort of traditional experiments can be saved. Numerically, the DOE approach was implemented for quantifying the individual and interactive effects between the blends' components, represented by argon, H₂O and CO₂ against both the products' properties and the mole fractions for both CO₂ and H₂O calculated by the Gaseq program, according to the design of the experimental matrix.

The final inspection in this procedure was to employ the CHEMKIN-PRO program, applying the GRI-Mech 3.0 chemical kinetics reaction mechanism, to give reliable results by providing different critical species for the one-dimensional combustor model [15]. This model was used to determine flame characteristics for

the final selected blends in a combustion process of a gas turbine. These mixtures were simulated through two clusters. The first cluster is called the Perfectly Stirred Reactor (PSR), consisting of the following three distinct zones: a mixing zone in which fuel is partially premixed, a flame region connecting directly to the previous zone, and the Central Recirculation Zone (CRZ), where the products of the combustion process are recirculated. The second cluster uses a Plug Flow Reactor (PFR) for post-flame operation along a 0.1 m duct.

3. Results and discussion

3.1. 0-D Chemical reaction analysis

The thermodynamic properties were calculated for each blend using the Gaseq program. In addition, a conventional methane-air mixture was used as a reference. These properties for products, including temperature, γ , c_p , with H₂O and CO₂ as products, were selected for blends against a range of equivalence ratios, as shown in the following Figs. 2 and 3.

The outlet temperatures for blend 58 (25-23-19) almost matched those obtained for the methane-air mixture, as shown in Fig. 2(a). In addition, other blends are either higher at around 100 degrees – blend 79 (24-19-19) and blend 109 (24-8-29) – or

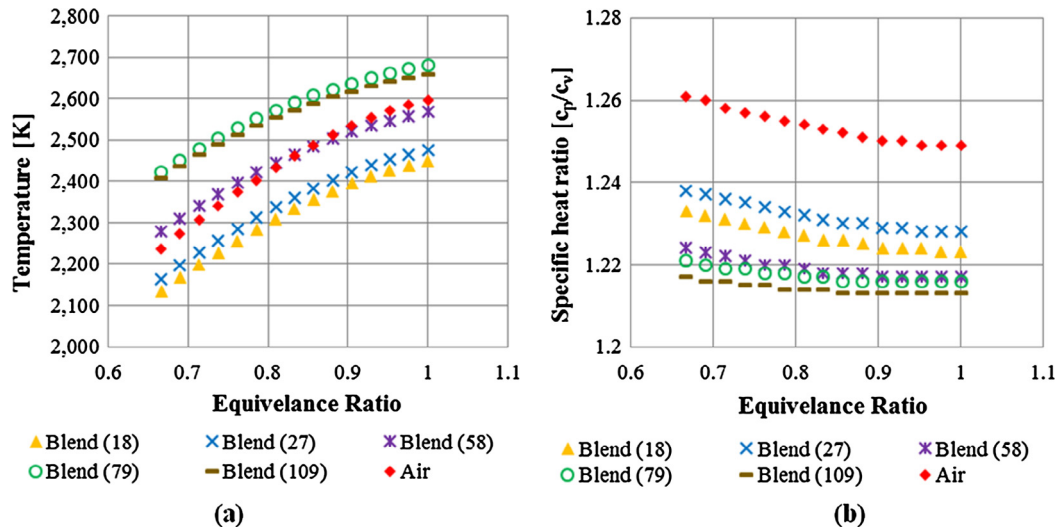
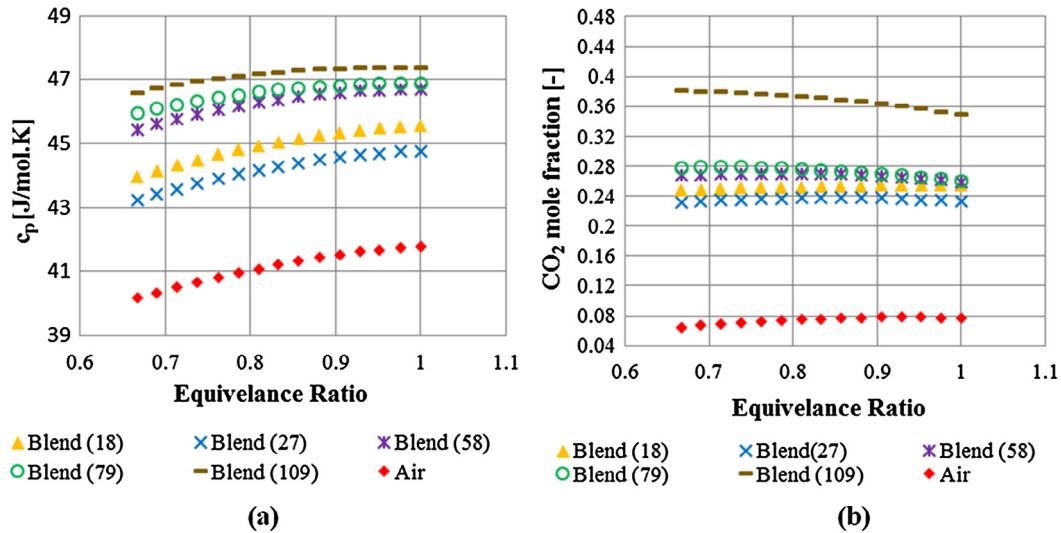


Fig. 2. Products of temperature and specific heat ratio for blends compared to air.

Fig. 3. Products of heat capacity and CO₂ for blends compared to air.

lower with an approximately similar range to the reference. Regarding specific heat ratio, the results indicate that this property is only about 2–4% below that obtained from air. Blend 58 (25–23–19) is nearly in the middle of this group, as shown in Fig. 2(b).

Moreover, heat capacity increases for all mixtures in comparison with air as a working fluid, as shown in Fig. 3(a), enhancing power output generation. Additionally, Fig. 3(b) indicates that the concentration of CO₂ products rises by around 40% compared with air. These mole fractions might enable mitigation of a portion of CO₂ emissions by condensing the water in the exhaust gas. The remainder of the CO₂ and inert gas in the exhaust would have to be recirculated in the OF combustion process.

The matrix shown in Table 1 was created using empirical data utilising results obtained from the Gaseq program. In this matrix, each thermodynamic property and the mole fraction of products for all of the generated blends were compared with their equivalent produced from the methane-air mixture used as a reference. As such, the eight blends tabulated represent the optimum blends out of all 120 cases. In the following Table 1, column 1 represents the blend's number, columns 2–4 indicate sequentially the mole fractions of Ar, H₂O and CO₂ while columns 5–7 represent the ther-

modynamic properties for these blends and the last two columns, 8 and 9, signify the mole fractions for both water and CO₂ products.

3.2. DOE analysis

Data provided by the DOE method shows whether thermodynamic properties with H₂O and CO₂ products were either affected positively or negatively by individual or interacting blend components. As illustrated in Fig. 4(a), outlet temperature responds inversely towards Ar, H₂O and CO₂. Fig. 4(b) illustrates that increased Ar correlates with increased specific heat ratio value, producing higher efficiency, while this property reacts inversely with both H₂O and CO₂.

3.3. Combustion characteristics

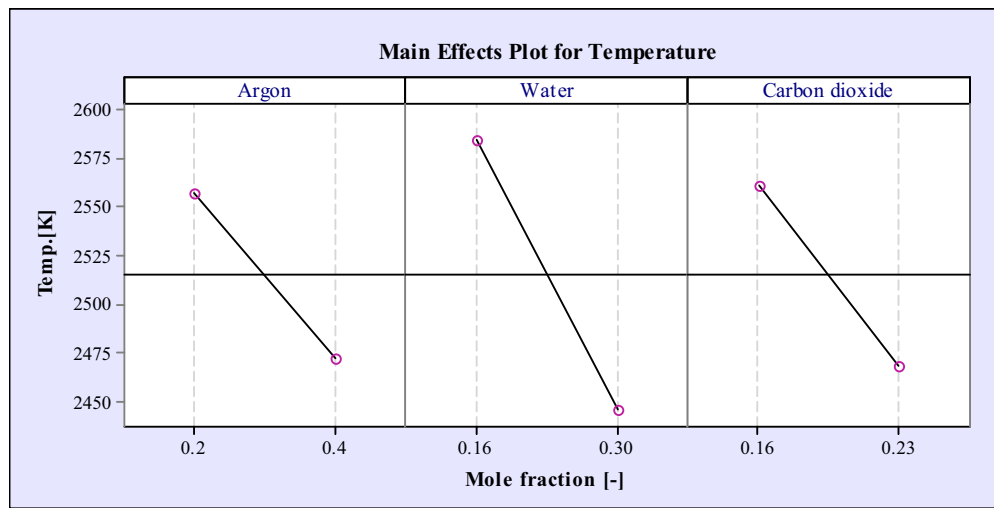
The Chemkin-PRO program initially tested the eight tabulated blends at 288 K with atmospheric pressure and equivalence ratio = 1. The flame characteristics of these mixtures were then simulated at industrial conditions similar to those of a gas turbine combustor, i.e. 10⁶ Pa. Subsequently, a comparison was made for

Table 1

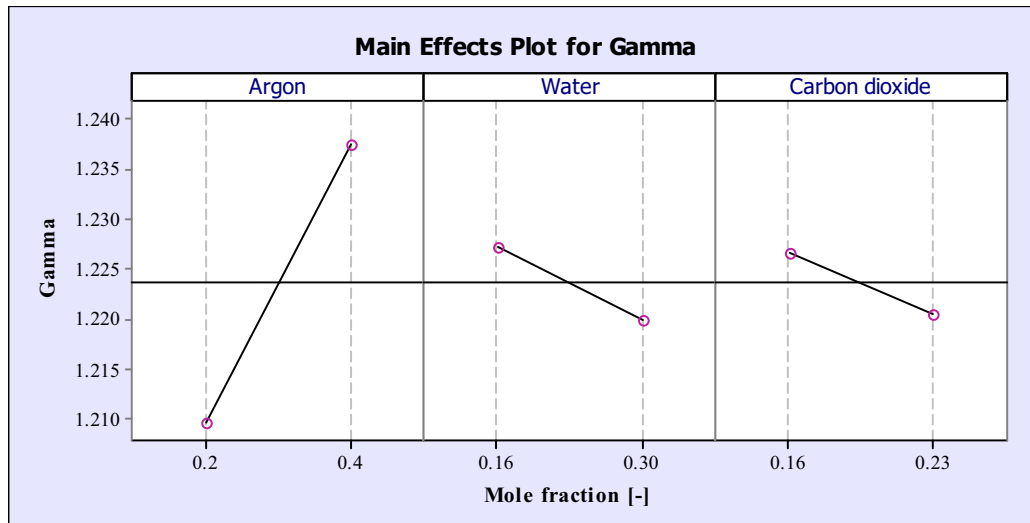
The optimum selected blends, using empirical data.

Blend	Ar [Mole fraction]	H ₂ O [Mole fraction]	CO ₂ [Mole fraction]	T (K)	c _p [J/mole K]	Gamma [c _p /c _v]	H ₂ O [Mole fraction]	CO ₂ [Mole fraction]
Air				2596.4	41.766	1.249	0.177	0.076
6	0.271	0.271	0.171	—	++	—	+++	++
18	0.287	0.251	0.179	—	+	—	+++	++
26	0.343	0.231	0.154	—	+	—	+++	+
27	0.307	0.244	0.162	—	+	—	+++	++
33	0.292	0.237	0.182	—	+	—	+++	++
58	0.251	0.230	0.188	0	++	—	+++	++
79	0.239	0.191	0.191	+	++	—	+++	++
109	0.242	0.084	0.290	0	++	—	++	+++

0: Same as reference; +: Greater than reference; ++: Considerably greater than reference; +++: Far greater than reference; —: Lower than reference; —: Considerably lower than reference; —: Far lower than reference.



(a)



(b)

Fig. 4. Temperature and specific heat ratio response towards Ar, H₂O and CO₂.

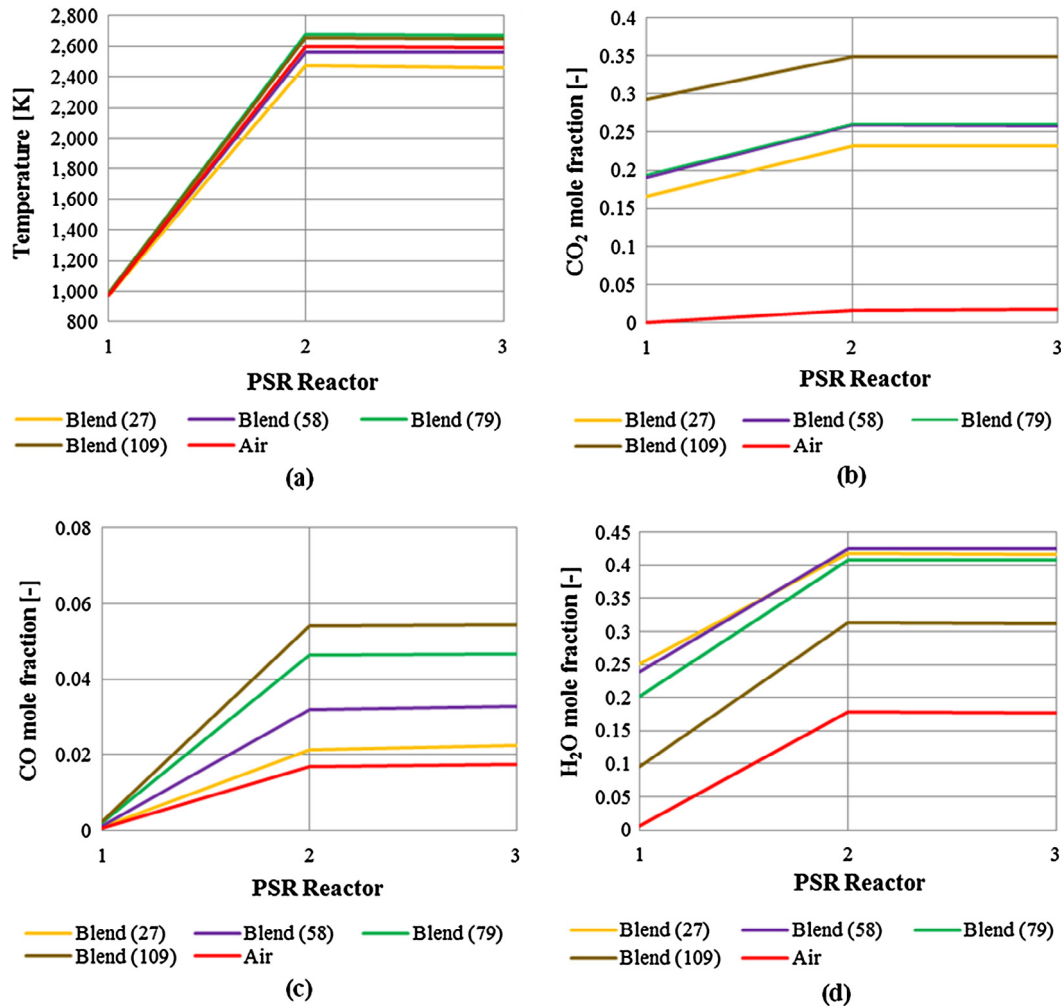
the eight flame values against the one obtained from the reference under the equivalent running conditions, for further investigations of those that have flame speeds close to the reference, as shown in Table 2.

Out of the eight blends, the chosen blends for further analysis were 58 (25-23-19), 79 (24-19-19), and 109 (24-8-29). Blend 27

(30-24-16) was also investigated, although its flame speed descends to around half the reference value. These four mixtures were compared according to characteristics obtained from the 1-D simulation approach in both the PSR and PFR clusters. Fig. 5(a) shows that the temperatures of blend 58 (25-23-19) are approximately equivalent to those produced by the current air cycle. Moreover,

Table 2Flame speed for selected blends with methane at 10^5 and 10^6 Pa, and $\phi = 1$.

Pressure condition (Pa)	Flame speed (m/s)								
	Pure methane	8 Optimum blends							
		27	58	79	109	33	26	18	6
10^5	0.431	0.218	0.312	0.453	0.384	0.217	0.203	0.201	0.204
10^6	0.151	0.797	0.127	0.212	0.178	0.723	0.640	0.650	0.676

**Fig. 5.** Temperature and mole fractions of CO_2 , CO and H_2O in a PSR.

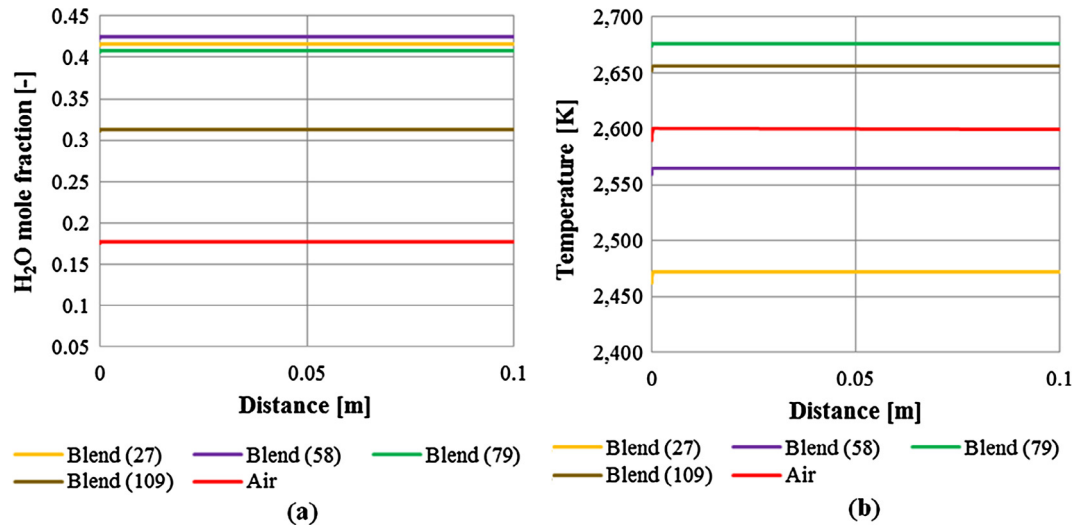
CO_2 concentration is elevated in the exhaust gas for this blend with the highest mole fractions of water vapor, for the recovery process and about 1.5 times more CO than conventional fuel as shown in Fig. 5(b)–(d).

Downstream of the reaction zone, the concentration of water remains high, resulting in a drop of ~ 40 K for the temperature of the exhaust gas for blend 58 (25-23-19), as shown in Fig. 6 (a) and (b). This figure also demonstrates that a blend, such as 27 (30-24-16), can still have acceptable product values under the combustion process. However, the considerable fall in the flame speed to 0.79 m/s leads to a higher propensity for blowoff. As such, a definition of the optimum CARSOXY blend requires a deep knowledge of its thermodynamic properties in a combustor and a comprehensive understanding of its flame and combustion characteristics. Thus, further research is required to demonstrate that the optimum blend, 58 (25-23-19), can be used under real gas turbine operating conditions.

4. Industrial gas turbine model for comparison

A simulation model was proposed for calculating the performance of a 3.9 MW Rolls-Royce Allison 501-KB5 industrial gas turbine. This model was used to calculate the generated power and the efficiency working with NG/air. Then, the results were correlated to those obtained from a real turbine running at equivalent fuel-air mixture under design (100% load) and off – design (90–10%) operating regimes [16]. This model for the gas turbine was utilised for comparing the optimum CARSOXY blend with oxygen/methane as reactants to NG/air running under stoichiometric working conditions.

In this numerical model, Eq. (2) was used to calculate the specific compression work. Then, the outlet temperature for the compressed air was determined by employing Eq. (3). After that, the heat capacity was ascertained from Eq. (4). Next, b , which represents the fuel/air mass flow rate ratio, was determined from Eq.

Fig. 6. Mole fraction of H₂O and temperature in a PFR.

(5). Following that, Eq. (6) was utilised for calculating the specific work for the industrial turbine. Finally, both heat supplied and the efficiency of the gas turbine were sequentially determined using Eqs. (7) and (8).

$$L_c = \bar{c}_{p_{air(1-2)}} \cdot T_1 \left(\Pi_c^{\frac{1}{\eta_{pc}} \frac{R_{air}}{c_{p_{air(1-2)}}}} - 1 \right) \quad (2)$$

$$T_2 = T_1 \cdot \Pi_c^{\frac{1}{\eta_{pc}} \frac{R_{air}}{c_{p_{air(1-2)}}}} \quad (3)$$

$$\frac{c_p(T)}{R} = \sum_{k=1}^{12} C_k \cdot \left(\frac{T}{1000} \right)^{k-6} \quad (4)$$

$$b = \frac{m_{fuel}}{m_2} = \frac{\bar{c}_{p_{gas(0-3)}} \cdot (T_{3t} - T_0) - \bar{c}_{p_{air(0-2)}} \cdot (T_{2t} - T_0)}{\eta_{cc} \cdot (LHV + h_{fuel}) - \bar{c}_{p_{gas(0-3)}} \cdot (T_{3t} - T_0)} \quad (5)$$

$$L_T = \bar{c}_{p_{gas-air(3-4)}} \cdot \frac{(1 - r_{air}) \cdot (1 + b) \cdot T_3 + r_{air} \cdot M \cdot T_2}{(1 - r_{air}) \cdot (1 + b) + r_{air}} \cdot \left(1 - \Pi_T^{\eta_{pT} \frac{R_{gas-air(3-4)}}{c_{p_{gas-air(3-4)}}}} \right) \quad (6)$$

$$q_{in} = \frac{1}{\eta_{cc}} \cdot (1 - r_{air}) \times \left[(1 + b) \cdot \bar{c}_{p_{gas-air(0-2)}} \cdot (T_{3t} - T_0) - \bar{c}_{p_{air(0-2)}} \cdot (T_{2t} - T_0) - b \cdot h_{fuel} \right] \quad (7)$$

$$\eta_{GT} = \frac{L_T \cdot \eta_m - L_c}{q_{in}} \quad (8)$$

5. Numerical results

The results show that the relative error for the power calculated by the mathematical model and the value of the real turbine was 0.22% while the relative error for the efficiency was 0.07%. Thus, the curves of these parameters approximately match, as shown in Fig. 7(a) and (b).

The numerical model was employed to test the performance of the same turbine running on blend 58 (25-23-19) with oxygen and methane as reactants. Then, NG/air results running in the same turbine were compared to those obtained from the blend. Both cases used stoichiometric conditions in each of the seven different cases presented in Fig. 8.

The specific output power produced by the 3.9 MW Rolls-Royce turbine working running the 58 CARSOXY blend is 219–244 kW

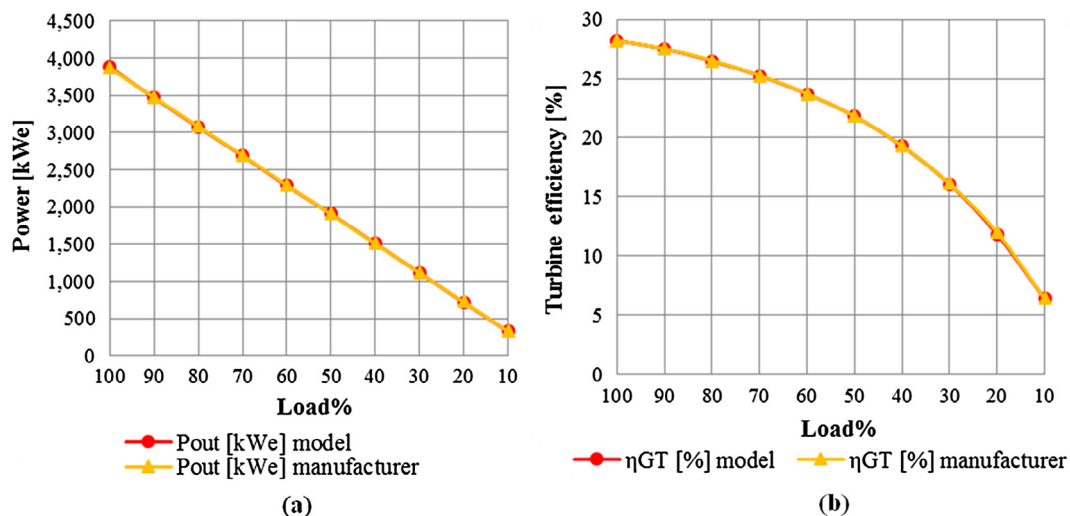


Fig. 7. Validation of power produced and efficiency.

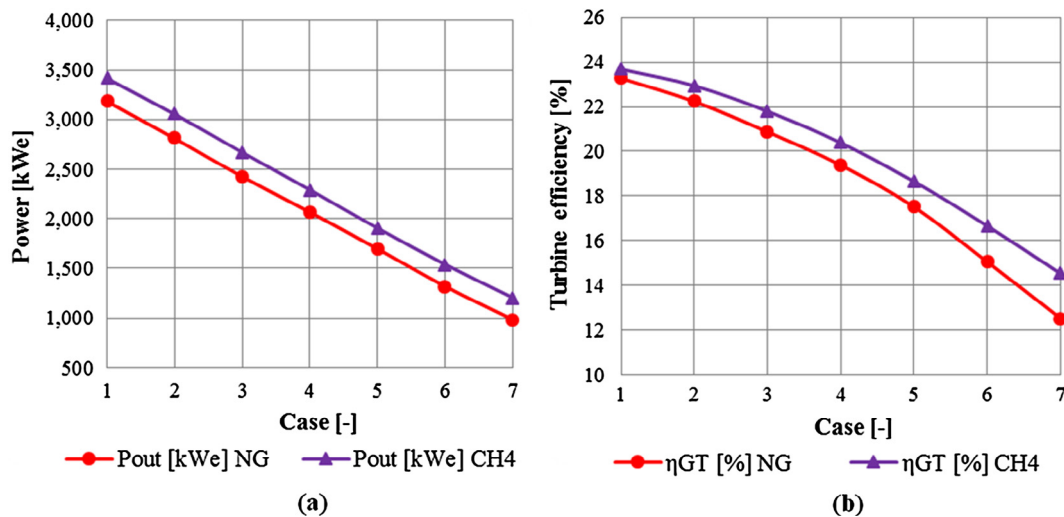


Fig. 8. The power produced and efficiency of the gas turbine working with CARSOXY blend for different mass flow rate cases compared to similar conditions for NG/air.

higher than the values obtained using NG/air, as shown in Fig. 8(a). Moreover, the efficiency of this industrial turbine working with CARSOXY is 1.75%–13.93% higher than that produced by NG/air. This comparison with NG/air as a working fluid is shown in Fig. 8(b).

6. Conclusion

This paper proposes a novel investigation for a combination of concepts, which were CCS technology integrated with oxy-fuel combustion and utilising steam with inert gas injections. The aim was to find an optimum CARSOXY blend that can be used instead of air as a working fluid. A mixture, consisting of 25%Ar–23% H_2O –19% CO_2 , has almost equivalent thermodynamic properties and flame speeds to air which was used as a reference.

As a result, the optimum blend could replace air in a combustion process in the EvGT cycles. Using CARSOXY blend 58 has improved outlet temperature and specific heat ratio, which leads to generating higher output power and efficiency than that of a conventional air cycle. The specific output power produced by the industrial Rolls-Royce gas turbine running blend 58 with methane and oxygen as reactant is between 219–244 kWe higher than that produced by NG/air. The efficiency of the turbine has also been improved by 1.75–13.93% using the optimum blend in comparison with NG/air as working fluid.

Additionally, this optimum CARSOXY blend has potential for producing efficient and powerful CCS-Oxyfuel combustion in gas turbines to maintain a clean environment. Employing this blend in gas combustors also mitigates emissions by recirculating CO_2 products in a combustion process and eliminates NO_x , since N_2 is not used.

Recommendations

Future work is recommended to employ a diffusive injection method to test the CARSOXY blend since no premixed combustion is needed. This experimental work could be carried out to ascertain the combustion characteristics of the optimum blend under actual operation conditions.

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